

Catalytic activity and stability of Y zeolite for phenol degradation in the presence of ozone

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Abstract

As a stable microporous material, de-aluminated Y zeolite has been used for the first time as an ozonation catalyst and showed remarkable activity for the removal of phenol and chemical oxygen demand (COD) in aqueous solution. The Y zeolite exhibited excellent repetitive-use performance even after continuous operation for 10 cycles. The ozone decomposition rate, influence of hydroxyl radical scavenger and influence of reaction temperature were investigated. The results indicate that Y zeolite accelerates the decomposition of ozone and the generation of hydroxyl radicals, consequently enhances the degradation of phenol and the removal of COD.

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1. Introduction

Aromatic compounds are common pollutants in the effluents of several industries. Among these substances, phenol is a compound typically produced in the petrochemical, chemical and pharmaceutical industries. Phenol has been classified as a priority pollutant in the United States Environmental Protection Agency (USEPA) list for its toxic, carcinogenic, mutagenic, teratogenic and non-biodegradable properties [1]. Recently, because of its importance as a pollutant considerable attention has been paid to chemical degradation of phenol [1–7].

Catalytic ozonation, being a strong oxidation process has attracted much attention in the wastewater treatment field [8–10]. Catalytic ozonation includes homogeneous catalytic ozonation and heterogeneous catalytic ozonation. The former is based on the catalysis of metal ions in aqueous solution, while the latter is based on the surface catalysis of solid-state catalysts. Compared with the homogeneous catalytic process, the main advantage of the heterogeneous catalytic ozonation is

the avoidance of secondary pollutants, as some ionized metals are considered toxic substances in water [11]. In the past few years, many heterogeneous catalysts have been utilized to improve the ozonation efficiency. Generally speaking, most of solid-state catalysts are metal oxides or metal oxides on supports [8,12]. However, a drawback of metal oxides catalyst is the leaching of metal ions. Because some short chain acids will always be generated in oxidation process of organic pollutants, the leaching of metal ions is difficult to avoid in the using of metal oxides catalyst, which results in the secondary pollution and the catalyst deactivation [13–15]. Therefore, it is highly desirable to develop environmental friendly ozonation catalysts with good stability as well as high activity.

De-aluminated Y zeolite, a well known ultra-stable microporous material [16–19], has been widely used as sorbent or catalyst support in various chemical reactions [18–21]. To the best of our knowledge, the application of Y type zeolite as ozonation catalyst in water treatment has not been reported. In this work, de-aluminated Y zeolite was developed as an ozonation catalyst for the degradation of phenol in water. Y zeolite revealed prominent catalytic activity and catalysis stability for the degradation of phenol and the removal of chemical oxygen demand (COD).

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2. Experimental section

2.1. Materials

The Y zeolite, de-aluminated by water vapor, which was used in this work was supplied by Fushun Research Institute of Petroleum and Chemicals, China. The framework Si/Al ratio of obtained sample was 3.83 characterized by X-ray diffraction (XRD) on an X'Pert PRO X-ray diffractometer (Philips, Netherlands), and specific surface area was $532 \text{ m}^2 \text{ g}^{-1}$ measured by BET method on an ASAP2020 surface area and porosity analyzer (Micromeritics, USA). The particle sizes of Y zeolite were about $0.5\text{--}1 \mu\text{m}$ according to transmission electron microscopy (TEM) images obtained with a JEM-200CX (JEOL, Japan) transmission electron microscope at an accelerating voltage of 200 kV.

All chemicals used such as phenol, catechol, hydroquinone, *p*-benzoquinone, *tert*-butanol, $\text{K}_2\text{Cr}_2\text{O}_7$ and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ were of analytical grade and were used without further purification. The water used throughout was distilled water.

2.2. Ozonation procedure

The catalytic degradation experiments of phenol were performed in a semicontinuous flow mode at 293 K. Ozone was generated in a laboratory ozone generator (self-made by Nanjing University) using pure oxygen as gas source. The flow rate of oxygen was 5 mL min^{-1} , and the flow rate of ozone was 0.30 mg min^{-1} . In a typical catalytic degradation procedure, 0.5 g of Y zeolite and 120 mL of simulated wastewater (the initial concentration of phenol was 100 mg L^{-1}) were mixed in a flask under stirring and thermostatic control. Then ozone was fed into the bottom of the flask with continuous stirring. At given intervals, 3.0 mL of samples were taken from the reactor and centrifuged for analytical determination. The control experiments of single ozonation (without catalyst) were carried out under the same conditions. The scheme of experimental set-up is shown in Fig. 1.

2.3. Analysis

The concentrations of phenol, and its oxidized intermediates such as catechol, hydroquinone and *p*-benzoquinone were determined by a LC-10AD high performance liquid chromatography (HPLC, Shimadzu) with a reversed-phase $4.6 \text{ mm} \times 250 \text{ mm C}_{18}$ waters column (Cosmosil, Japan) at room temperature. The elution was carried out by pumping the mixture of methanol and water (5:5, v/v) at a flow rate of 1.0 mL min^{-1} , and an attached SPD-10A UV-vis detector (Shimadzu) was used. The wavelengths were set at 210, 274, 288 and 246 nm for the analysis of phenol, catechol, hydroquinone and *p*-benzoquinone, respectively.

The values of COD were obtained through oxidation with $\text{K}_2\text{Cr}_2\text{O}_7$ under acidic conditions and titrate analysis with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ aqueous solution according to the national criterion of PR China [22]. The relative concentrations of ozone in water were determined with a UV-vis spectrophotometer

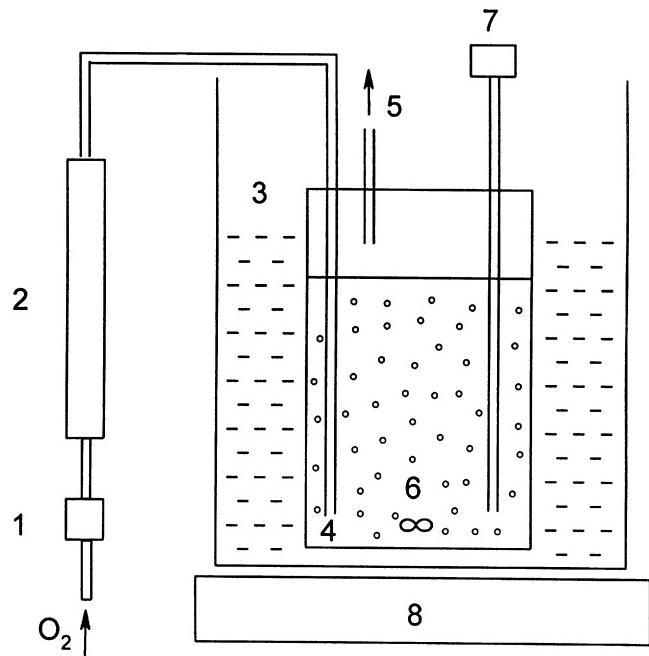


Fig. 1. Scheme illustration for the experimental set-up of catalytic ozonation: (1) Airflow meter, (2) ozone generator, (3) thermostatic bath, (4) airflow intake, (5) airflow outtake, (6) magneton, (7) sampler and (8) magnetic stirrer.

(752, Shanghai, China) by recording the absorption at 258 nm in a 1 cm quartz cell [6,23].

3. Results and discussion

3.1. Catalyst activity

In order to distinguish the catalysis and the adsorption on Y zeolite, a set of preliminary experiments were performed using an initial concentration of phenol of 100 mg L^{-1} . In the first experiment, 0.5 g of Y zeolite and 120 mL of simulated wastewater was mixed, and only oxygen (no ozone generation) was fed into the flask at a rate of 5 mL min^{-1} for 60 min. After this time, the residual concentration of phenol was 99.5 mg L^{-1} . The second experiment aimed at determining the amount of the adsorption of ozonation degradation products. Firstly, 120 mL of 100 mg L^{-1} phenol solution (initial COD was 254 mg L^{-1}) was subjected to a single ozonation for 60 min. Then 0.5 g catalyst was added into this solution and stirred for 30 min without ozone. The values of COD before the mixing and after the mixing were 156 and 151 mg L^{-1} , respectively. These results indicated that the adsorptions of phenol and its degradation products on Y zeolite were few, which hardly affected the concentration of phenol and the value of COD.

As mentioned in Section 2.2, the ozonation of phenol in the absence and presence of Y zeolite were carried out. Fig. 2A shows the degradation of phenol along with ozonation time in single ozonation and catalytic ozonation. It can be seen that the Y zeolite revealed remarkable catalysis on the ozonation degradation of phenol in water. For example, the residual concentration of phenol was 42.0 mg L^{-1} after single ozonation for 45 min, while the residual concentration of phenol in

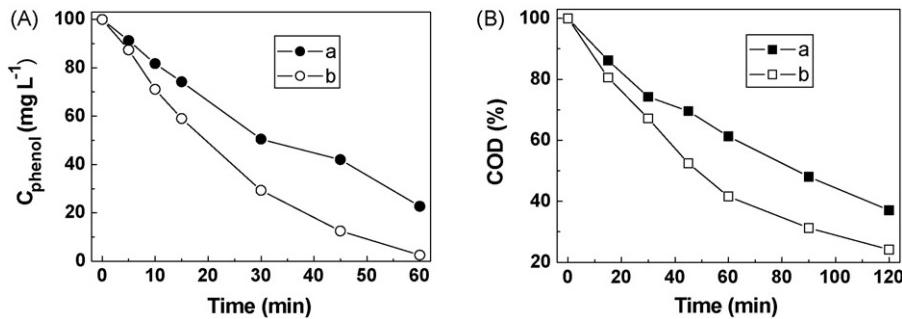


Fig. 2. Degradation of phenol (A) and removal of COD (B) along with ozonation time: (a) single ozonation and (b) catalytic ozonation. Catalyst dose: 0.5 g; volume of wastewater: 120 mL; reaction temperature: 293 K; initial concentration of phenol: 100 mg L^{-1} ; flow rate of oxygen: 5 mL min^{-1} ; flow rate of ozone: 0.30 mg min^{-1} .

catalytic ozonation merely was 12.5 mg L^{-1} . The degradation efficiency of phenol increased about 50.9% due to the catalysis of Y zeolite relative to single ozonation.

It is known that the removal of COD denotes the elimination degree of organic pollutants, which is an important goal in water treatment. In this experiment, the influence of Y zeolite on the removal rate of COD was measured as shown in Fig. 2B (in which COD % means the ratio of residual value to original value). It was found that the Y zeolite had notable effect on removal of COD. For instance, the removal value of COD from 30.4% in single ozonation increased to 47.5% in catalytic ozonation for 45 min. It was also seen that the removal efficiency of COD increased about 56.3% relative to the single ozonation due to the catalysis. Because COD comes from the summation of phenol and its degraded intermediates, in catalytic process, the removal efficiency of COD increased more (56.3%) than that of phenol (50.9%). When the ozonation time proceeded to 120 min, the COD removal of 75.8% could be achieved in catalytic ozonation process.

Before being degraded to small organic acids, phenol is easily oxidized to more toxic compounds such as catechol, hydroquinone and *p*-benzoquinone [4,6,24–26]. Thus, the time-dependent concentrations of these intermediates in single ozonation and catalytic ozonation were investigated, respectively. The results are shown in Fig. 3. It can be found that, the changing tendencies of three intermediates were similar, and the concentrations of them in catalytic ozonation were higher than those in single ozonation at the first 30 min. Along with the ozonation process, the concentrations of these intermediates in catalytic ozonation descended quickly. When the ozonation time reached 60 min, the concentrations of catechol, hydroquinone and *p*-benzoquinone in catalytic process were 0.42 , 0.58 and 0.46 mg L^{-1} , respectively, which were lower than those in single ozonation. The results indicated that, besides the removal of phenol and the COD, the catalyst was also helpful for the degradation of these toxic intermediates. Consequently the Y zeolite exhibited high catalytic activity for the ozonation degradation of phenol.

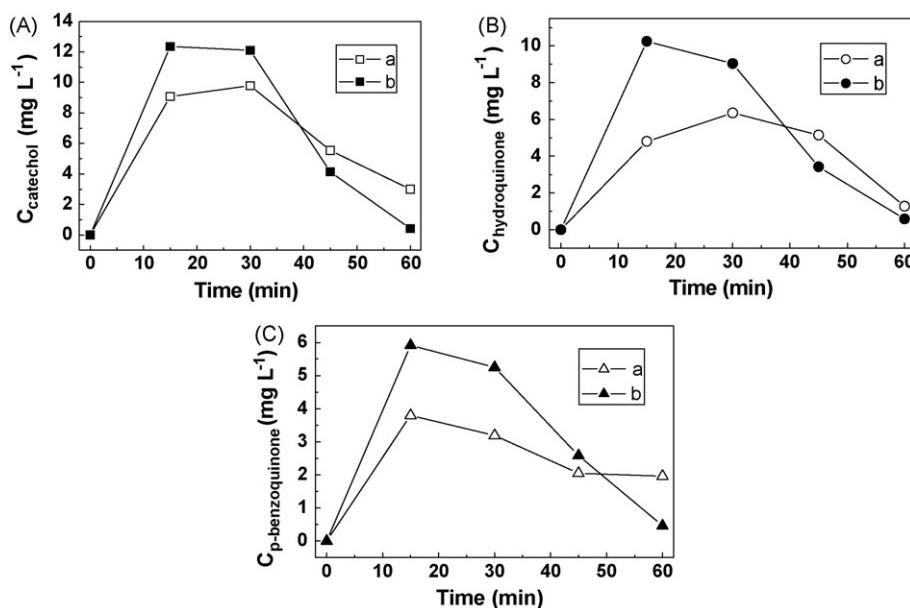


Fig. 3. Time evolution of concentrations of catechol (A), hydroquinone (B) and *p*-benzoquinone (C): (a) single ozonation and (b) catalytic ozonation. Catalyst dose: 0.5 g; volume of wastewater: 120 mL; reaction temperature: 293 K; initial concentration of phenol: 100 mg L^{-1} ; flow rate of oxygen: 5 mL min^{-1} ; flow rate of ozone: 0.30 mg min^{-1} .

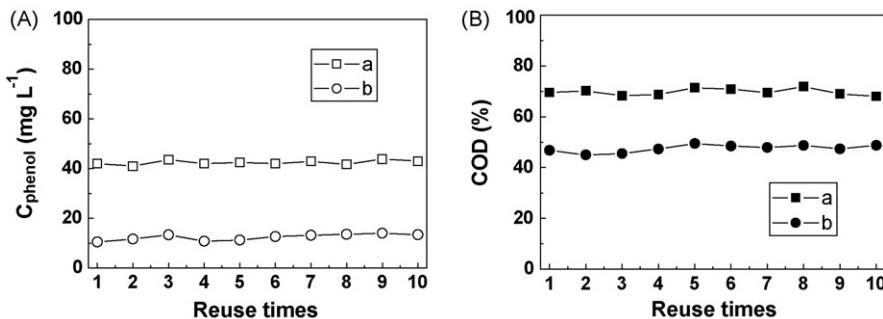


Fig. 4. Degradation of phenol (A) and removal of COD (B) in reuse experiment: (a) single ozonation and (b) catalytic ozonation. Catalyst dose: 1.0 g; volume of wastewater: 120 mL; reaction time: 45 min; reaction temperature: 293 K; initial concentration of phenol: 100 mg L^{-1} ; flow rate of oxygen: 5 mL min^{-1} ; flow rate of ozone: 0.30 mg min^{-1} .

3.2. Reuse performance of catalyst

When the practical application of Y zeolite is considered, the long-time catalytic efficiency is of great importance. In order to evaluate the stability of catalyst activity, the reuse experiment was carried out. In this experiment, 1.0 g de-aluminated Y zeolite was used in 120 mL of wastewater with initial concentration of 100 mg L^{-1} , and the ozonation time was fixed at 45 min in every process. After the ozonation process, the suspension was centrifuged. The clear solution was used for analytical determination, and the Y zeolite was collected and used directly in next catalytic ozonation process. The same process was repeated for 10 times.

The degradation of phenol and the removal of COD in reuse experiment are shown in Fig. 4. From the results, it can be seen that the catalytic activity of Y zeolite kept constant and no obvious deactivation was observed. It is well known that the de-aluminated Y zeolite possesses good hydrothermal stability [27]. It may be said that the steady long-time catalytic efficiency of Y zeolite is correlative to the stationary framework of Y zeolite. Therefore, the de-aluminated Y zeolite shows considerable promise for practical application in water treatment.

In addition, when we compared the degradation efficiency in Fig. 4 (catalyst dose 1.0 g in 120 mL) with that of 45 min in Fig. 2 (catalyst dose 0.5 g in 120 mL), it can be found that the difference was not remarkable. This may be explained that, under certain conditions (reaction temperature, initial concentration, ozone flow, agitation speed, etc.), there is a limitation for the degradation of phenol and the removal of COD.

3.3. Influence of catalyst on ozone decomposition

We know that the catalytic ozonation was always related to the interaction between catalyst and ozone [8]. In order to study this interaction, the effect of Y zeolite on the decomposition of ozone in water was tested. In this experiment, 0.5 g of de-aluminated Y zeolite was added into 120 mL of ozone-saturated solution, and the mixed suspension was stirred continuously. After certain intervals, samples were taken and centrifuged quickly for analytical determination. Under the same conditions, the decomposition of ozone alone (without

catalyst) in water was also recorded for comparison. As shown in Fig. 5, the presence of Y zeolite obviously accelerated the decomposition of ozone. The results indicate that there is an interaction between ozone and the catalyst. In general, the Y zeolite is considered to be a polar sorbent which can easily

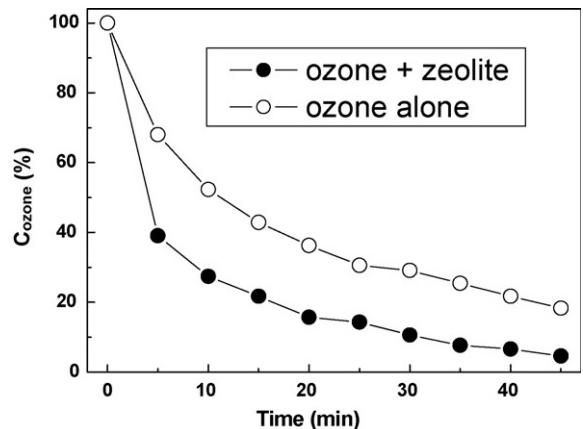


Fig. 5. Decomposition of ozone in water along with time. Catalyst dose: 0.5 g; volume of water: 120 mL; temperature: 293 K; flow rate of oxygen: 5 mL min^{-1} ; flow rate of ozone: 0.30 mg min^{-1} .

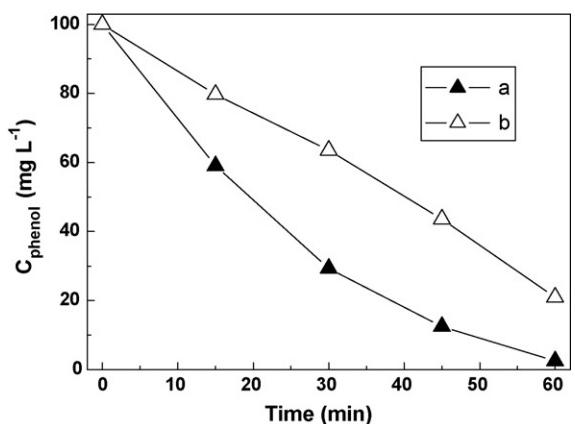


Fig. 6. Influence of hydroxyl radical scavenger (tert-butanol) on the catalytic degradation of phenol: (a) no *tert*-butanol and (b) with *tert*-butanol added. Catalyst dose: 0.5 g; volume of wastewater: 120 mL; addition of *tert*-butanol: 0.3 g; reaction temperature: 293 K; initial concentration of phenol: 100 mg L^{-1} ; flow rate of oxygen: 5 mL min^{-1} ; flow rate of ozone: 0.30 mg min^{-1} .

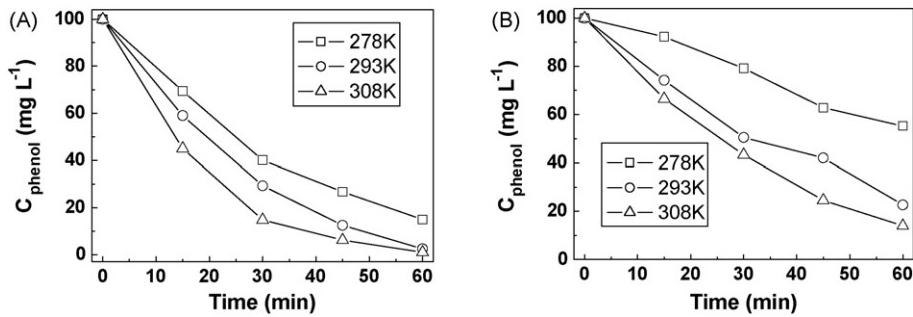


Fig. 7. Influence of reaction temperature on the catalytic degradation (A) and the single ozonation (B) of phenol. Catalyst dose: 0.5 g; volume of wastewater: 120 mL; initial concentration of phenol: 100 mg L⁻¹; flow rate of oxygen: 5 mL min⁻¹; flow rate of ozone: 0.30 mg min⁻¹.

adsorb polar molecules [28]. Ozone molecule, which can react as a dipole and a nucleophilic agent, is very unstable in water [8]. When it nears to Y zeolite, it may be adsorbed preferentially on the zeolite framework and dissociate subsequently. Therefore, it may be said that Y zeolite is advantageous for the adsorption and the decomposition of ozone.

3.4. Influence of hydroxyl radical scavenger

According to traditional catalytic ozonation theory, molecular ozone can oxidize organic substances via a direct route or can undergo decomposition via a chain reaction mechanism to produce free hydroxyl radicals [8]. In above section (influence of catalyst on ozone decomposition), it has been proved that catalyst accelerated the decomposition of ozone in water. In order to demonstrate the role of hydroxyl radical in the degradation of phenol, the influence of hydroxyl radical scavenger was investigated. Because *tert*-butanol is easy to react with hydroxyl radical ($k = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and difficult to react with molecular ozone ($k = 3.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$), it has been widely used as a probe to determine the role of hydroxyl radicals in degradation of pollutants [8,12,29,30]. Therefore *tert*-butanol was introduced here. In this experiment, 0.3 g of *tert*-butanol was added to 120 mL of reaction system with other reaction conditions kept constant.

Fig. 6 shows the influence of *tert*-butanol on the catalytic ozonation degradation of phenol. It can be found that the addition of *tert*-butanol had obvious negative effect on the catalytic degradation of phenol. The results suggested the important role of hydroxyl radicals in catalytic ozonation. Combined with the effect of catalyst on the ozone decomposition, it can be concluded that the catalyst accelerated the decomposition of ozone and enhanced the generation of hydroxyl radicals hence accelerating the degradation of phenol and the removal of COD.

In addition, the degradation of phenol in the presence of *tert*-butanol (curve b in Fig. 6) may be explained that, because molecular ozone was excessive, phenol could still be oxidized by ozone molecule. That is, phenol was oxidized by both hydroxyl radicals and molecular ozone in catalytic ozonation.

3.5. Influence of reaction temperature

The influence of reaction temperature on the catalytic degradation of phenol was investigated, and the control experiment of single ozonation was also carried out. The reaction temperature was controlled at 278, 293 and 308 K, respectively. Fig. 7A illustrates the catalytic degradation of phenol at different temperatures and clearly indicates that the degradation rate of phenol was accelerated with the increase of reaction temperature. It may be explained that, although the concentration of ozone in water decreases with the rising of temperature, the generation rate of hydroxyl radical from ozone molecule is faster at higher temperature. Therefore, hydroxyl radicals played an important role in the degradation of phenol, because the degradation of phenol by hydroxyl radical is much faster than that by ozone molecule [30,31].

As shown in Fig. 7B, the degradation of phenol in single ozonation was also increased with the rising of temperature. After the single ozonation of 45 min at 278, 293 and 308 K, the removal of phenol were 37.2, 58 and 75.4 mg L⁻¹, respectively. While after the catalytic ozonation of 45 min at 278, 293 and 308 K, the removal of phenol were 73.3, 87.5 and 93.8 mg L⁻¹. Then, the degradation efficiencies of phenol were increased about 97%, 51% and 24% at 278, 293 and 308 K due to the catalysis of the Y zeolite. By comparing these results, it is found that the Y zeolite exhibited certain catalysis activity at different temperatures, and the increased degradation efficiency of phenol in the presence of Y zeolite was the highest at lower temperature of 278 K.

4. Conclusions

In conclusion, the de-aluminated Y zeolite has been successfully used as an ozonation catalyst for the degradation of phenol. Y zeolite exhibited high catalytic activity and nonexpendable performance for the ozonation degradation of phenol and the removal rate of COD, owing to the stable framework structure of de-aluminated Y zeolite.

By investigating the ozone decomposition rate, influence of hydroxyl radical scavenger and influence of reaction temperature, it was shown that the Y zeolite could accelerate the transformation from ozone molecules to hydroxyl radicals, which is essential for a catalyst. Due to the interaction between

ozone and Y zeolite, the decomposition of ozone and the generation of hydroxyl radicals were accelerated, and the degradation of phenol and the removal of COD were enhanced. As a catalyst, the de-aluminated Y zeolite has supplied a feasible and environmental friendly choice for the catalytic ozonation of phenol in wastewater.

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